



Behaviors of radical fragments in tar generated from pyrolysis of 4 coals

Wenjing He^a, Zhenyu Liu^{a,*}, Qingya Liu^{a,c,*}, Donghui Ci^b, Caroline Lievens^b, Xiaofen Guo^b

^a State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China

^b Coal Upgrading Center, National Institute of Clean-and-Low-Carbon Energy, Beijing 102209, China

^c Department of Chemistry, Northwestern University, Evanston, IL 60208, USA



HIGHLIGHTS

- Coal pyrolysis tars contain radicals at a level of 10^{17} spins/g.
- Coal tars generate more radicals and coke at temperature of 623 K or higher.
- The coke formed in the coal tars contains radicals at a level of 10^{19} spins/g.
- The coke formation in the tars follows the 2nd order kinetics with E_a of 200 kJ/mol.
- The coal tars are relatively more stable than biomass tars.

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ABSTRACT

Fast pyrolysis, with high heating rates and short retention time, was studied extensively in past decades due to high liquid yields. Although many fast pyrolysis processes have been developed and tested, few were reported to be successful on commercial scale due to problems including poor tar quality and system plugging. It is, therefore, important to exam the reactivity of the fast pyrolysis tars particularly at temperatures they may experience upon releasing from the coal surface. Four coals of different ranks were pyrolyzed to study the reactivity of the tars. It is found that the tars contain high concentrations of radicals and are highly reactive at temperatures higher than 623 K to generate more radicals and form coke. The coke formed in the tars contributes most of the radicals in the tar samples. The coking behavior can be expressed by the second order kinetics with activation energies of around 200 kJ/mol. The coal tar's reactivity is significantly less than that of biomass tars obtained from the same pyrolysis reactor under the same conditions.

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1. Introduction

Pyrolysis of coal has been applied on large scales to produce coke, tars (oil and chemicals), and coke oven gas for more than a century. Successful technologies are those characterized by slow heating rates and long pyrolysis time although they were believed to result in low tar yields. To increase tar yields, fast pyrolysis with heating rates in a range of $10\text{--}10^4$ K/s and reaction time in seconds has been studied in past decades worldwide [1–3]. The aim of the fast heating and fast cooling was to avoid the secondary reactions, such as retrogressive or condensation reactions, as much as

possible because they were considered to be the main reasons for the low tar yields [4–6]. Many fast pyrolysis processes have been developed and tested with this understanding but few were reported to be successful on commercial scale. The main problems of these fast pyrolysis processes were poor oil quality and severe system plugging due to deposition of cement-like materials in the product lines [7–9]. The failing of extensive efforts in reactor modification and product separation in solving these problems indicates that new insight should be gained to solve the problems especially on the fundamental chemistry involved.

It is well recognized that pyrolysis of coals follows a radical mechanism [10], starting with thermal cleavage of covalent bonds to generate volatile radical fragments and following by coupling of the radical fragments to form stable products [11–14]. Many works have tried to monitor radicals in coal pyrolysis and to correlate them with pyrolysis conditions [15,16], however, most of them focused on radicals in the solids (the raw feeds and the char) with limited attention on radicals in the tars [17]. Since the coupling of

* Corresponding authors. Address: Box 35, Beijing University of Chemical Technology, China. Tel.: +86 10 64421073; fax: +86 10 64421077 (Z. Liu). Address: Department of Chemistry, Northwestern University, Evanston, IL, 60208 USA. Tel.: +1 847 491 2982 (Q. Liu).

E-mail addresses: liuzy@mail.buct.edu.cn (Z. Liu), qingya.liu@northwestern.edu (Q. Liu).

radicals is governed by the probability of the radicals to get close to each other, fast pyrolysis may reduce the extent of the coupling reactions in the reactor and consequently result in more radicals in the tars and more radical reactions in the product lines [18,19], which are closely related to the poor quality and stability of the tars and plugging of the product lines.

In this work, we show radical concentration of tars obtained from pyrolysis of four coals in a temperature range from room temperature to 813 K, and report detailed changes in radical concentration of the tars heat treated at various temperatures to study the reactivity of the tars. The temperatures are those the tars would experience in large scale reactors and pyrolysis systems upon their release from the coal surface, including the high temperature product lines or the volatile/solid separation units, or in the heating units of tar refining. Kinetics of the coke formation in the tars under these high temperature conditions is also studied.

2. Experimental

The four coals studied are Hulunbeier coal (HLBE), Bulianta coal (BLT), Buertai coal (BET) and Daliuta coal (DLT), all from China. The coals were ground to sizes of 100–140 mesh and dried at 383 K in a vacuum for 4 h. The proximate and ultimate analyses of the coals were determined and shown in Table 1.

The details of pyrolysis experiments, electron spin resonance (ESR) tests, and heat treatment of the tars have been described elsewhere [20]. Briefly, the pyrolysis experiments were carried out in a tubular reactor, shown in Fig. 1, under a flow of N₂ at 200 mL/min with a heating rate of 80 K/min and a final temperature of 813 K. The residence time of the volatiles is about 3 s in the furnace zone before being condensed into tar. The tar was sampled by a capillary of 1 mm in diameter and then weighed, sealed in a glass tube suitable for the ESR test, and then stored in liquid nitrogen. The char was cooled to room temperature in N₂, sampled into the capillary and weighed, and then sealed in the glass tube suitable for the ESR test. All the ESR tests were carried out at room temperature, and the temperatures of the samples were controlled at room temperature during the test. The capillary and the glass tube showed little influence on ESR measurement. To simulate the high temperature environment the tars would experience, upon their release from the coal surface, in a large scale reactor or pyrolysis systems, the tars (sealed in glass tubes) were subjected to a heat treatment, i.e. kept in a heating jacket maintained at 293, 373, 473, 573, 623, 673, 723 or 773 K for 4 h. The radical concentrations of the tars kept at these temperatures were tested at 0.5, 1, 2, 3 and 4 h of the heat treatment. The tar samples were then extracted by tetrahydrofuran (THF) for 12 h after the glass tubes been cut open at the two ends. The THF insoluble matters staying in the capillaries, termed coke, were quantified after being dried at 348 K in a vacuum for 4 h. The coke yield, defined as the mass of the coke divided by the mass of tar sample in percentage, were determined. The radical concentrations of the coke staying in the capillaries were also determined by ESR.

Table 1
Proximate and ultimate analysis of the raw materials.

Raw materials	Proximate analysis (wt.%)				Ultimate analysis (wt.%, daf)					
	Coal	Symbol	M _{ad}	A _{ad}	V _{ad}	C	H	O ^a	N	S
Hulunbeier	HLBE		30.99	9.10	29.94	73.93	5.12	19.43	1.14	0.38
Bulianta	BLT		13.04	12.34	30.55	79.76	4.85	13.92	1.06	0.40
Buertai	BET		5.13	14.77	31.11	80.44	4.77	13.57	1.02	0.20
Daliuta	DLT		4.89	6.11	28.97	82.02	4.58	11.90	0.92	0.59

Note: ad: air dry; daf: dry-and-ash-free basis.

^a By difference.

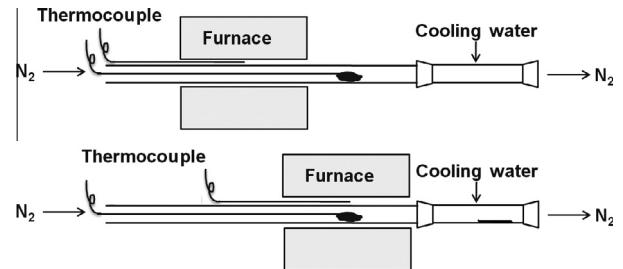


Fig. 1. The schematic diagram of the pyrolysis apparatus.

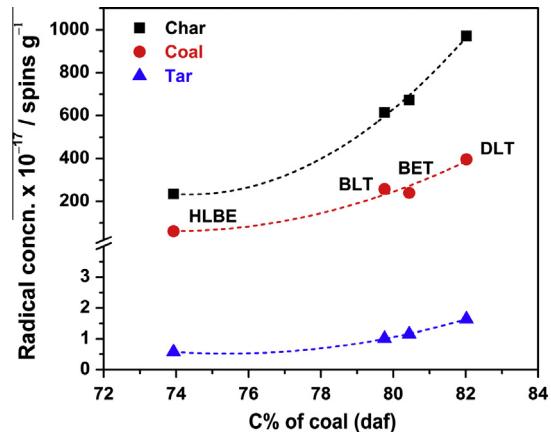


Fig. 2. Radical concentrations of the four coals and their pyrolysis products.

3. Results and discussion

3.1. Radical concentrations of the coals and the pyrolysis products

Fig. 2 shows the radical concentrations of the four coals and their pyrolysis products, chars and tars. It is clear that the radical concentrations of the coals, chars, and tars all increase with an increase in coal rank, namely the % of the coals. The radical concentrations of the coals are about 10¹⁸–10¹⁹ spins/g, which agree well with that reported by Retcofsky for American coals [21]. The radical concentrations of the chars are in the level of 10¹⁹ spins/g, which are higher than that of the corresponding coals. The radical concentrations of the tars are in a level of 10¹⁷ spins/g, which are much lower than that of the coals and the chars.

In principle and in the simplest case, the thermal cleavage of a covalent bond in coal may generate two radical fragments, which are both volatiles or one of them is volatile while another one is non-volatile. If contact between the non-volatile and the volatile radical fragments is limited, one would expect that the radical concentration of the char is higher than that of the coal. This is the case shown in Fig. 2. This estimation also indicates that the number of

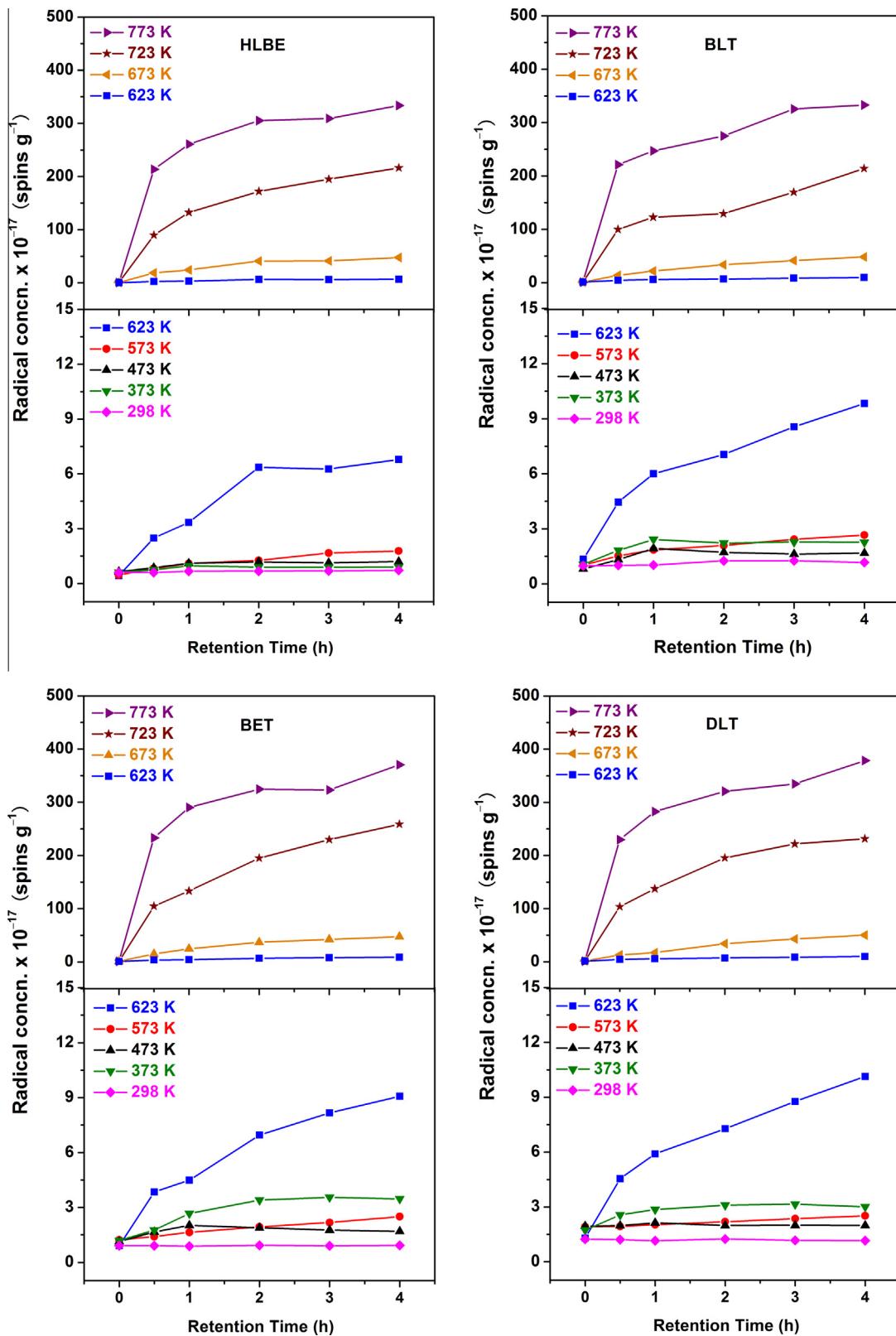


Fig. 3. Radical concentrations of the tars experienced to various temperatures.

volatile radical fragments should be more than that of the char radicals. The huge difference in radical concentration between the chars and the tars further suggests that more than 99% volatile radical fragments generated in the pyrolysis underwent coupling

reaction before the volatiles being condensed, if few radical is in the gas products.

Although the radical concentrations of the tars are much lower than that of the coals and chars, they are much higher than that of

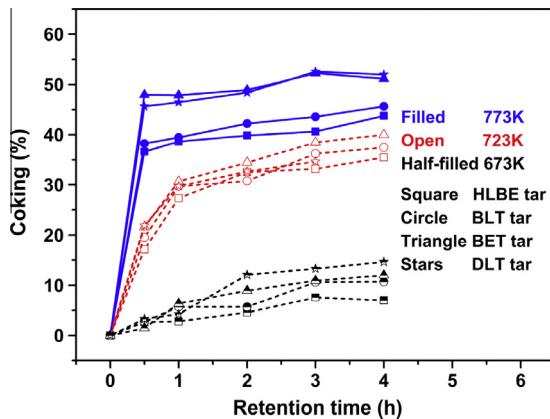


Fig. 4. The amounts of coke formed in the tars at various temperatures in 4 h.

commercial fuels (such as diesel and gasoline that contain few radical, measured in this work), crude oils (10^{14} – 10^{16} spins/g) [22], and direct coal liquefaction liquids (10^{16} spins/g) [18]. The high radical concentration of tars had been reported to be responsible for the high reactivity of tar in air, or aging, which results in increases in tar viscosity [20,23], change in color and in other physical properties [24]. Clearly, the existence of the large amounts of radical fragments in coal tars is responsible for their poor stability and poor quality.

3.2. Behavior of tars subjected to heat treatment

Fig. 3 shows radical concentrations of the four tars kept at various temperatures. It can be seen that the radical concentrations of the tars show a similar trend, change slightly, no more than three times, at temperatures of 573 K and lower, increase with an increase either in temperature or in time at temperatures of 623 K and higher, and reach a level of more than 2×10^{19} spins/g at 723 K in 30 min. These results indicate that the coal tars contain some weak covalent bonds that undergo cracking at temperatures of 623 K and higher, even though the pyrolysis experiments were carried out to 813 K. This behavior is easy to understand considering that the heating rate of the pyrolysis reactor is about 80 K/min (1.3 K/s) and the residence time of the volatiles in the furnace zone is about 3 s. These conditions allow the volatiles to experience only a maximum of 4 K increase in temperature before being cooled. For example, the tars generated at 600 K may experience a maximum temperature of 604 K before being cooled, their cracking at temperatures higher than 604 K, therefore, is possible.

It is rather surprising to see in Fig. 3 that the radical concentration of the tars increases to high levels and maintains there in 4 h, indicating that the radicals in the tars do not undergo coupling reaction. The only logical explanation to this is that these radicals are not accessible to each other. It is also found visually that black solid matter forms in the capillary during the heat treatment especially when the temperatures are higher than 623 K. To find out whether the solid formation in the tars and the high radical concentrations of the tars are related, the tars underwent the 4 h heat treatment are subjected to THF extraction to quantify THF insoluble matters, which is termed coke. The results in Fig. 4 show that the tars contain little coke initially, and coke forms during the heat treatment. The amount of the coke formed increases with increases in temperature and time, reaching 40% in 30 min at 773 K, for example. Furthermore, the trends in coke formation in Fig. 4 are similar to that in radical concentration in Fig. 3, suggesting that these behaviors are likely interrelated with each other.

The presence of coke in the tars suggests that each of the tar samples subjected to the heat treatments is actually a mixture of

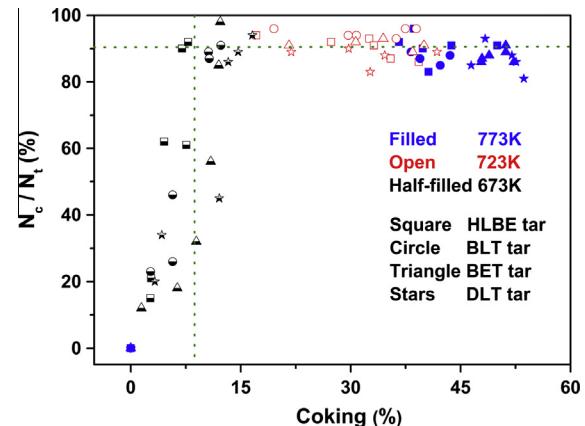


Fig. 5. The contribution of coke radicals (N_c) to the total radicals in the tar samples (N_t) at various coke contents.

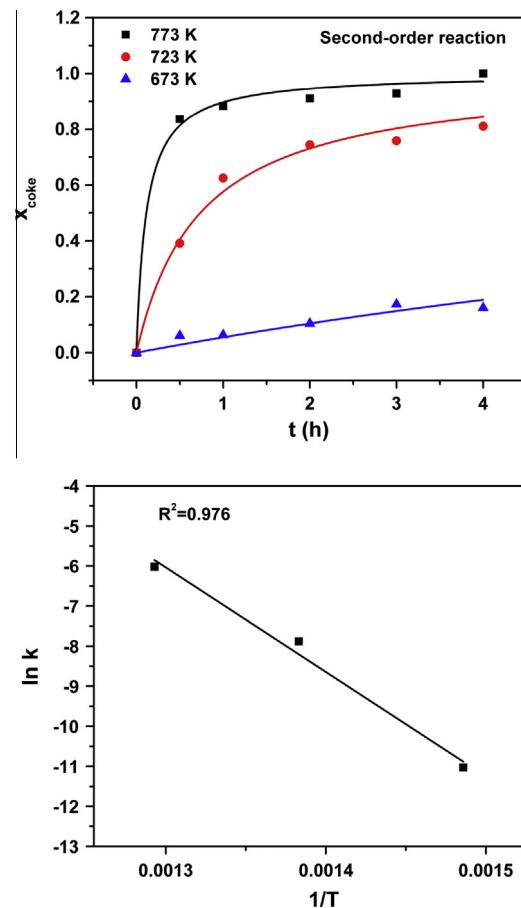


Fig. 6. The second order kinetics fitting to coking data of HLBE coal tar in Fig. 4.

a liquid and a solid, and the radical concentration of each tar sample in Fig. 3 may involve radicals contributed by the liquid as well as by the solid. Since the radical concentrations of the tars are usually lower than 10^{18} spins/g [18,20,22,23], which are less than many data shown in Fig. 3, especially those heat treated at 723 and 773 K, the radical concentrations of the solid are likely to be high. To verify this deduction, the amount of radicals in each of the coke samples in Fig. 4 is measured, termed N_c , and compared with the total radicals of the corresponding tar sample in Fig. 3, termed N_t , in the form of N_c/N_t . The data in Fig. 5 shows that the

ratio N_c/N_t has a close relation with the coke content of the tar sample. At coke contents of 0–8 wt.%, N_c/N_t increases approximately in a rate of 10% per 1 wt.% coke. For coke contents of greater than 8 wt.%, about 90% of the total radicals are contributed by coke. Since very small coke particles may be carried away from the capillaries by THF during the extraction, it is possible that most of the radicals in a tar sample are that of coke even at very low coke contents.

The presence of large amounts of radicals in tar-derived coke is a phenomenon that is not well understood, although a similar behavior has been reported by Singer and Lewis in a study of carbonization of pitch, they attributed the increase in radical concentration to radicals concentrated in higher molecular weight components [25]. It seems to us that the formation of the large amounts of radicals in coke may be attributable to two factors: (1) Cracking of the tars at temperatures of 623 K and higher to generate more radical fragments. (2) Many of the radical fragments generated from cracking of the tars contain more than one unpaired electrons, and coupling of one of the electrons with another radical fragment may form a structure that makes the rest of the unpaired electrons inaccessible to other radical fragments, especially when the products of the coupling are large in molecular size.

3.3. The kinetics of coke formation in tars

The discussion presented above shows that coking of the tars is significant at temperatures higher than 673 K, and the trend of the coke formation is clear. Coking kinetics therefore is estimated to better understand the properties of the tars. Regression was made to fit various kinetic models to the data in Fig. 4. Among the models tested, including the first order, second order and other orders, the best fit is obtained by the second order kinetics, which is expressed as Eq. (1), where x_{coke} is the ratio of the "mass of coke formed in tar at time t " against "the mass of coke formed in tar at time ∞ (approximated by the maximum coke formed at 773 K in Fig. 4)", and k is the rate constant. The k can be expressed by Arrhenius Equation, Eq. (2), where k_0 is the frequency factor, E_a the apparent activation energy, R the gas constant, and T the temperature.

$$\frac{dx_{\text{coke}}}{dt} = k(1 - x_{\text{coke}})^2 \quad (1)$$

$$\ln k = \ln k_0 - E_a/RT \quad (2)$$

The fitting results for HLBE coal tar are shown in Fig. 6 as an example, and the activation energy and the frequency factor for each of the four coal tars are listed in Table 2. It is noted that the activation energies of the four tars for coking are similar, ranging from 199 to 218 kJ/mol. These values indicate that the properties of the tars are in between of a light petroleum residue and a heavy petroleum residue because the activation energies for cracking of these fractions are 188 and 230 kJ/mol, respectively, as reported by Radmanesh et al. [26]. These activation energies may also indicate that the tars are mixtures of various components, including saturate + aromatics and resins + asphaltenes because the activa-

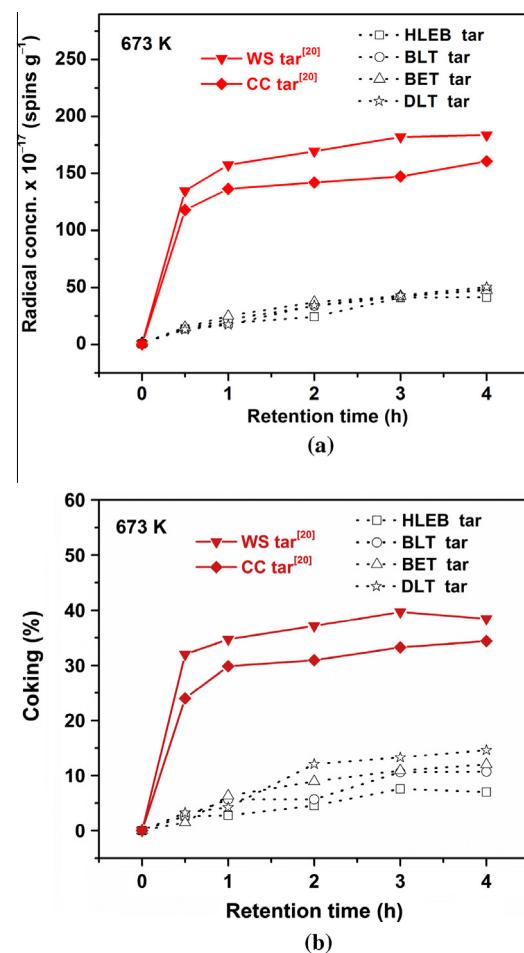


Fig. 7. Comparison the radical concentration (a) and coking yield (b) of the coal tars with that of biomass tars at 673 K.

tion energy of the former is 120–220 kJ/mol at high conversions while that of the latter is 220–300 kJ/mol, as reported by Gonçalves et al. [27].

3.4. Comparison of coal pyrolysis tars with biomass pyrolysis tars

The coking behavior of the coal tars shown in Fig. 4 is compared with that of biomass tars derived from pyrolysis of walnut shell (WS) and corncob (CC) reported earlier by us using the same apparatus and following the same experiment procedures [20]. Fig. 7 shows radical concentrations (a) and coking behaviors (b) of the four coal tars and the two biomass tars at 673 K as an example. It is clear that the amounts of radicals and coke formed in the biomass tars are 3–4 times higher than that in the coal tars under the same conditions, even though the radical concentrations of the biomass tars are lower than that of coal tars before the heat treatments, indicating that the coal pyrolysis tars are relatively more stable than the biomass tars.

4. Conclusions

The tars generated from pyrolysis of four coals in a tubular reactor and a temperature ramping mode to 813 K with a volatiles residence time of 3 s in the furnace zone are studied. The tars contain radicals with concentrations of 10^{17} spins/g and are active to generate more radicals at temperatures higher than 623 K, reaching 10^{19} spins/g at 723 K in less than 30 min, for example. This

Table 2

Parameters of second-order kinetics for coking of the tars.

Tars	Activation energy (kJ/mol)	Frequency factor ($\times 10^{-3} \text{ s}^{-1}$)	Correlation coefficient
HLBE	218	7.7	0.976
BLT	199	7.0	0.987
BET	211	7.5	0.999
DLT	202	7.1	0.992

increase in radical concentration of the tars is accompanied by the formation of THF insoluble matters, coke. About 90% of the total radicals formed in tar in the temperature range studied are contributed by the coke when the coke content is higher than 8 wt.%. The coking behavior can be expressed by the second order kinetics with activation energies of around 200 kJ/mol. The coal tars are relatively stable than biomass tars due to less radical and coke formation under the same conditions.

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References

- [1] Gibbins-Matham J, Kandiyoti R. Coal pyrolysis yields from fast and slow heating in a wire-mesh apparatus with a gas sweep. *Energy Fuels* 1988;2:505–11.
- [2] Dadyburjor DB, Liu Z, Davis BH. Coal liquefaction. In: James DH, Castor WM, editors. *Kirk-Othmer encyclopedia of chemical technology*. New York: John Wiley and Sons Inc; 2011. p. 24–7.
- [3] Tyler RJ. Flash pyrolysis of coals. I. Devolatilization of a Victorian brown coal in a small fluidized-bed reactor. *Fuel* 1979;58:680–6.
- [4] Stiles HN, Kandiyoti R. Secondary reactions of flash pyrolysis tars measured in a fluidized bed pyrolysis reactor with some novel design features. *Fuel* 1989;68:275–82.
- [5] Unger PE, Suuberg EM. Molecular weight distributions of tars produced by flash pyrolysis of coals. *Fuel* 1984;63:606–11.
- [6] Gönenc ZS, Fowler TG, Kandiyoti R, Bartle KD. Correlation of tar yields from a fixed bed coal pyrolysis reactor with in-situ esr-spin population measurements. *Fuel* 1988;67:848–52.
- [7] Howard JB. Fundamentals of coal pyrolysis and hydropyrolysis. In: Elliott MA, editor. *Chemistry of coal utilization*. New York: John Wiley and Sons, Inc; 1981. p. 665–784.
- [8] Edwards JH, Schluter K, Tyler RJ. Upgrading of flash pyrolysis tars to synthetic crude oil: 1. First stage hydrotreatment using a disposable catalyst. *Fuel* 1985;64:594–9.
- [9] Bridgwater AV. Review of fast pyrolysis of biomass and product upgrading. *Biomass Bioenergy* 2012;38:68–94.
- [10] Petrakis L, Grandy DW. Formation and behaviour of coal free radicals in pyrolysis and liquefaction conditions. *Nature* 1981;289:476–7.
- [11] McMillen DF, Malhotra R, Nigenda SE. The case for induced bond scission during coal pyrolysis. *Fuel* 1989;68:380–6.
- [12] Shi L, Liu Q, Guo X, He W, Liu Z. Pyrolysis of coal in TGA: extent of volatile condensation in crucible. *Fuel Process Technol* 2014;121:91–5.
- [13] Shi L, Liu Q, Guo X, Wu W, Liu Z. Pyrolysis behavior and bonding information of coal-A TGA study. *Fuel Process Technol* 2013;108:125–32.
- [14] Solomon PR, Fletcher TH, Pugmire RJ. Progress in coal pyrolysis. *Fuel* 1993;72:587–97.
- [15] Seehra MS, Ghosh B, Mullins SE. Evidence for different temperature stages in coal pyrolysis from in situ esr spectroscopy. *Fuel* 1986;65:1315–6.
- [16] Bolton C, Snape CE, O'Brien RJ, Kandiyoti R. Influence of carrier gas flow and heating rates in fixed bed hydropyrolysis of coal. *Fuel* 1987;66:1413–7.
- [17] Fowler TG, Bartle KD, Kandiyoti R. Limitations of electron spins resonance spectroscopy in assessing the role of free radicals in the thermal reactions of coal. *Energy Fuels* 1989;3:515–22.
- [18] Rudnick LR, Tueting D. Investigation of free radicals produced during coal liquefaction using ESR. *Fuel* 1984;63:153–7.
- [19] Mohan D, Pittman CU, Steele PH. Pyrolysis of wood/biomass for bio-oil: a critical review. *Energy Fuels* 2006;20:848–89.
- [20] He W, Liu Q, Shi L, Liu Z, Ci D, Lievens C, et al. Understanding the stability of pyrolysis tars from two biomass in a view point of free radicals. *Bioresour Technol* 2014;156:372–5.
- [21] Retcofsky HL, Stark JM, Friedel RA. Electron spin resonance in American coals. *Anal Chem* 1968;40:1699–704.
- [22] Elofson RM, Schulz KF, Hitchon B. Geochemical significance of chemical composition and ESR properties of asphaltenes in crude oils from Alberta. *Canada Geochim Cosmochim Acta* 1977;41:567–80.
- [23] Usman R, Khan R. Role of free radical chemistry on oxidative stability of coal pyrolysis liquids. *Fuel Process Technol* 1989;22:151–8.
- [24] Yamada Y, Matsumura A, Kondo T, Ukegawa K, Nakamura E. Free radicals formed in hydrotreated coal liquid and influence of oxygen. *Pet Sci Technol* 1984;2:165–76.
- [25] Singer LS, Lewis IC. ESR study of the kinetics of carbonization. *Carbon* 1978;16:417–23.
- [26] Radmanesh R, Chan E, Gray MR. Modeling of mass transfer and thermal cracking during the coking of Athabasca residues. *Chem Eng Sci* 2008;63:1683–91.
- [27] MLA Gonçalves, DAP Mota, WV Cerqueira, D André, LM Saraiva, MIF Coelho, et al. Knowledge of petroleum heavy residue potential as feedstock in refining process using thermogravimetry. *Fuel Process Technol* 2010;91:983–7.